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Elwha River sediments: phosphorus dynamics under diverse environmental conditions

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Elwha River Sediments: Phosphorus Dynamics under Diverse Environmental Conditions

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MASTER'S THESIS

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Emily Cavaliere

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A Thesis
Presented to
The Faculty of
Western Washington University

In Partial Fulfillment
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Abstract:

Two large dams on the Elwha River, on the Olympic Peninsula in Washington State, are scheduled for removal in 2011. Removing the Glines Canyon Dam will release up to 10.6 million cubic meters of sediment from Lake Mills. The sediments will be exposed to new physical and chemical conditions and be redistributed throughout the ecosystem. In the summer of 2008, sediment samples were taken from the above-water delta and the submerged lake bottom of Lake Mills to identify initial physical and chemical characteristics relating to the variable status of phosphorus in the sediments. The sediments were analyzed for different forms of phosphorus (P), amorphous iron (Fe), carbon (C), nitrogen (N), and particle size. The lake sediments had greater concentrations of all elements analyzed and had smaller mean particle size compared to the delta sediments. A two-week incubation of sediments under various environmental conditions indicated P release was not affected by atmosphere type. For delta sediments, P release was greater in freshwater than saltwater throughout the incubation, while for lake sediments this occurred only initially. Overall, the magnitude of P release was similar for the two sediment types. An isotherm study performed in conjunction with the incubation study revealed that both the lake and delta sediments could immobilize large quantities of added P, but lake sediments maintained dissolved P concentrations at half the level of delta sediments. Managers could use the information found in this study to help understand the phosphorus release and immobilization patterns in sediments after dam removal.

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1.0 Introduction

The Glines Canyon and Elwha dams on the Elwha River of the Olympic Peninsula, Washington State are scheduled for removal between 2011 and 2012 (Cornwall 2009). The goal of removing these dams is to restore the ecosystem for salmon habitat. These dams hold massive amounts of sediment in their reservoirs, Lake Aldwell and Lake Mills. Because more sediment is built up in Lake Mills, it was chosen as the research site for my study. Upon dam removal these sediments will be exposed to new physical and chemical conditions.

Some sediments will remain in place and become dewatered. Others will move downstream and become deposited within channels or on floodplains. Some will be transported into the Strait of Juan de Fuca. Larger particles will tend to erode less and be transported shorter distances than smaller particles. An unknown amount of P is currently attached to the Lake Mills sediments, and the different particle sizes are likely to contain different amounts of P (Selig 2003).

Lowering of the lake level will expose sediments to oxygenated conditions, whether they remain in place or are transported downstream. Exposure to oxygen can lead high rates of P immobilization under most circumstances through the binding of P onto amorphous Fe. However, biological activity may increase, increasing the likelihood of P release (Christophoridis and Fytianos 2006). For dewatered, redistributed, and redeposited sediments, P release could support vascular plant growth. Alternatively, the sediments could remain a sink, restrict P availability, and make colonization of exposed sediments unlikely (Kalff 2002, p. 341).

Phosphorus is often a limiting nutrient in oligotrophic water, like Lake Mills, because P is strongly associated with the sediment rather than the water column (Kalff 2002, p. 247). Suspended sediments may transport P and release some within the water column. Some of the sediment may reach the Strait of Juan de Fuca, a marine environment. Marine systems tend to be N limited, and P sufficient (Caraco et al. 1990). Many studies have found that P availability in marine sediments is not influenced by changes in oxygen (Gunnars and Blomqvist 1997). However, the concentrations of chloride and sulfate anions influence P dynamics through the exchange of the anions for the phosphate in Fe-bound P, releasing P (Caraco et al. 1990).

The objectives of this study were to characterize P in Lake Mills sediments and determine the likely factors that influence P dynamics before and after dam removal. The following hypotheses were evaluated:

Hypothesis 1: Fine sediments have higher concentrations of P than do coarse sediments.

Hypothesis 2: Exposure of sediments to oxic conditions decreases P release into water.

Hypothesis 3: Exposure of sediments to saltwater increases P release into water.

Lake Mills sediments were characterized to aid in the understanding of their P dynamics. Particle size, C and N were measured as baseline information about the sediments. Amorphous Fe was analyzed because of its potential interaction with P in sediments. A chemical fractionation scheme was used to quantify different forms of P: calcium (Ca) bound P, Fe bound P, organic P, and total P. These forms are important for understanding the

release and immobilization of P in Lake Mills sediments. Ability to immobilize P was determined with a sorption isotherm study.

The sediment characterization was complemented with a short-term incubation study to simulate P response to different environmental conditions that could occur after the dams are removed. The incubation study was an attempt to determine how the redox potential, salt concentrations, sediment types and time influence P release.

My study of P in Elwha River sediments has several unique facets. The Elwha River is oligotrophic; in contrast, most studies of P dynamics are conducted in systems that are eutrophic (Munn et al. 1999). My study gives us the opportunity to study a system before it is dramatically changed by the dam removals. Phosphorus dynamics in this type of unpolluted setting have rarely been studied before and could give insight in comparing unpolluted waters to polluted or eutrophic waters. My study is also unique because it is separated into two parts. The first part is the characterization study, which gives insight into how P dynamics work in The Elwha River system. The characterization study is then paired with the incubation study. The incubation study gives an idea of the magnitude and conditions of P release in water under varied environmental conditions. The combination of these two studies gives us a better perspective of P dynamics in the Elwha River sediments than the two studies separately.

2.0 Background

2.1 The Elwha System

The Elwha River flows north into the Strait of Juan de Fuca from the Olympic Mountains. Eighty-three percent of the area of the Elwha River watershed is within in the Olympic National Park (Munn et al. 1999). The upper reaches of river receive 560 cm of annual precipitation, while the lower reaches receive only 142 cm of precipitation. During the winter, the peak flood events average 31,000 m^3/s, while in the summer base flows average 150 m^3/s (Shaffer et al. 2006). The Elwha River was once known for its salmon runs including coho (*Oncorhynchus kisutch),* sockeye (*O. nerka),* pink (*O. gorbuscha),* chum (*O. keta),* steelhead trout (*O. mykiss,* summer and winter runs), and chinook salmon (*O. tshawytscha* spring and fall runs). Dam construction has depressed salmon runs (Duda et al. 2008).

The soils in the Olympic Mountains area influence the character of the sediments entering Lake Mills. The soils are under udic or perudic conditions, which speeds up the process of weathering (Wilson et al. 1996). The soil overlying basalt is considered to belong to the Andisols soil order. The sediment entering Lake Mills will then likely have andic characteristics (Karen Bennett, USDA Forest Service, personal communication). Andisols that do not have volcanic parent material, like those in the Elwha system, occur under cool, humid climates, (Buol et al. 2003). Andic properties include having organometallic and aluminosilicate compounds, high percentage of glass, medium to low percentages of clay and high percentage of organic matter and tend to be acidic. From the perspective of P dynamics, the most interesting characteristic of Andisols is the ability of the soil to fix added P, which

maintains low concentrations of P in the soil solution (Buol et al. 2003, p. 236). Andisols have a high affinity for P because P reacts with aluminum or Fe minerals to form Al or Fe phosphates (Negrin et al. 1998). The influence of andic properties on the sediments of the Elwha River could be large, reducing the amount of P available for plant and algal growth.

The Elwha and Glines Canyon dams were installed as run-of-the-river dams for hydroelectric purposes. A run-of-the-river dam has the same amount of water entering the system as leaves the system. Construction was finished in 1913 on the Elwha Dam, and 1927 on the Glines Canyon Dam (Duda et al. 2008). The dams change the hydrological and ecological characteristics of the river, which lead to changes in river flow, channel incision, restriction of channel migration, and changing water temperatures. The upper river no longer supports salmon because the dams were not constructed to allow for fish passage, and downstream of the dams the riparian and aquatic habitats have been altered. All of these changes have led to a complex degradation of the Elwha River system (Duda et al. 2008). Between dam construction and 1994, 10.6 million cubic meters of sediment accumulated behind Glines Canyon Dam and 2.98 million cubic meters behind the Elwha Dam (Mussman et al. 2008). The sediments have changed the structure of the lakes through delta creation and and new lake bed formation through sediment deposition. Some of the sediment will be released into the environment when the dams are removed.

In 1992 Congress passed the Elwha River Ecosystem and Fisheries Restoration Act (PL 102-495). The act directed the Secretary of the Interior to restore the Elwha River ecosystem and anadromous fisheries. After researching how to restore the ecosystem, the National Park Service decided that the only way to restore the ecosystems was to remove the dams (Duda et al. 2008). However, after removal, the sediments behind the dams will pose a problem for the

restoration of the ecosystem. My study is an effort to understand how those sediments could affect the ecosystem.

There are few studies documenting nutrients in the Elwha River system. The USGS report by Munn et al. (1999) report that the there is very little phosphate in the water column. Twenty-one sites had less than the detection limit of 10.0 µg/L of orthophosphate, three additional sites had up to 21.0 µg/L of orthophosphate, and no spatial pattern was observed where the presence of P was detected.

2.2 Importance of Phosphorus in Lakes and Reservoirs

Phosphorus is a chemically reactive element that is required for cellular processes of all life. In lakes and reservoirs algae are the most common primary producers. Algae require a certain concentration of phosphorus to grow. Their growth and death provide the system with organic matter and fixed nutrients, like N and P. However, with high levels of primary productivity, the lake water becomes opaque with all the algal cells. High levels of organic matter settle to the lake bottom, where decomposition happens. With high levels of decomposition of algal organic matter, oxygen is used during respiration, creating areas of low oxygen (Gächter and Wehrli 1998). Low oxygen levels can spread from beyond the lake bottom causing poor living conditions for the rest of the lake's flora and fauna. This is a common occurrence in lakes that are well to overly nourished, or eutrophic. These systems have high concentrations of N and P. Highly polluted regions all over the world have problems with eutrophication and over production leading to low oxygen levels and poor productivity (Kalff 2002, p. 94). Changing environmental conditions could affect specific forms of P and transfer large quantities of P to the water column.

Opposite an eutrophic system is an oligotrophic system or poorly nourished system. Lakes and reservoirs are usually found to be poor in P, while having sufficient concentrations of N, thus the limiting nutrient is P. Oligotrophic lakes/reservoirs are poor in nutrients and have low inputs of autochthonous organic matter, resulting in limited biological activity (Kalff 2002, p. 21). The Elwha River is an oligotrophic system as characterized by Munn et al. (1999). Lake Aldwell and Lake Mills on the Elwha River, consequently, have low levels of soluble reactive P (SRP), which is usually interpreted as P available for algal growth.

After the dams are removed, plant growth on dewatered and redeposited sediments with low concentrations of P could be limited, preventing bank stabilization and colonization with native plant species. Transfer of P between sediments and water column under changed environmental conditions could alter P availability and productivity in the river.

2.3 Phosphorus in Lakes and Reservoirs

Many processes contribute to P dynamics in lakes and reservoirs. Phosphorus enters lakes and reservoirs through the incoming water and sediment load, as aggregate minerals, or organic detritus (Fig 1A). The P leaves the lake/reservoir as orthophosphate, which is a major component of SRP, suspended aggregate minerals, or as living algal cells and algal detritus. Within lakes, the P cycle oscillates between the water column and sediments (Fig. 1, Table 1B). Phosphorus becomes part of the sediment system through deposition of decaying organic detritus (allochthonous or autochthonous), deposition of eroded aggregate minerals from soils, and through the adsorption of P onto eroded and newly formed aggregate minerals. Within the sediments, the major forms of P are Fe-bound P, Ca-bound P, and organic P (Christophoridis and Fytianos 2006).

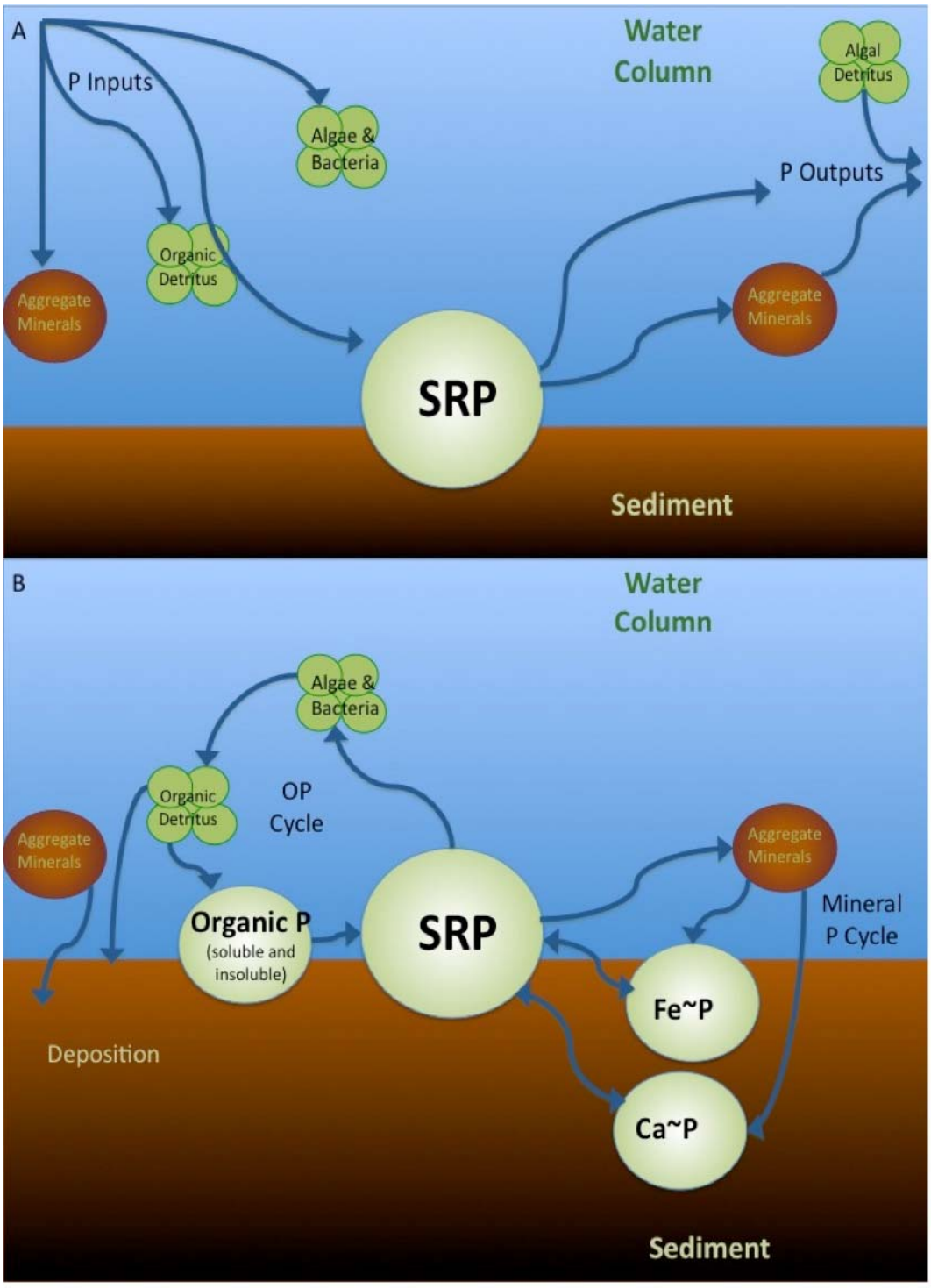

Figure 1. The simplified P cycle in a lake or reservoir. Figure 1A. is of the inputs and outputs of P in the system, Figure 1B is the P cycling between sediment and water column. The forms of P most commonly found in a lake system are bound in the green circles, soluble reactive P (SRP), Ca-bound P (Ca~P), Fe-bound P (Fe~P) and organic P. This figure also shows deposition of organic detritus and aggregate minerals, the organic P cycle, the mineral cycle and the inputs and outputs of P.

Table 1. Forms of P in simplified lake P-cycling model. Analytical approach is from Ruban et al. 1999a.

Abbreviation	Phosphorus Form	Description	Analytical approach to estimate form
SRP	Soluble reactive phosphorus	Dissolved orthophosphate, dissolved reactive polyphosphates, and dissolved reactive organic P	React with antimonyl-tartrate-molybdate
SOP	Soluble organic P	Soluble organic phosphorus	
Algal P	Algal P	Phosphorus in live algae	
OP	Particulate Organic P	Phosphorus in detritus and humic substances	Extract with hydrochloric acid after ashed at 450°C
Ca~P	Particulate Ca-bound P	Phosphorus in tricalcium phosphate, chlorapatite, hydroxyapatite, carbonate fluorapatite, biogenic apatite, and apatite of igneous or metamorphic origin	Extract with hydrochloric acid
Fe~P	Particulate Fe, Al, Mn-bound P, FeOOH≈P	Phosphorus in Fe phosphate, and orthophosphate immobilized onto Fe, amorphous Fe, aluminum, and manganese (Mn) oxides	Extract with sodium hydroxide

2.3.1 Soluble forms of P

Soluble P is present in the sediment porewater and water column. Soluble reactive P (SRP) encompasses orthophosphate, and some polyphosphates and soluble organic P (SOP). There may be small amounts of nonreactive organic P as well (Pulatsu and Topcu 2009). Mortimer (1941) discusses soluble organic matter diffusing from sediment, which could include soluble organic P. Monbet et al. (2009) suggest that SOP may play an important role in P cycling in lakes as well as SRP. Soluble organic phosphorus can be broken down into three functional groups, labile phosphate monoesters, phosphate diesters and phytic acid, all three can be hydrolyzed by microbes, phytoplankton and zooplankton (Monbet et al. 2009). Nonreactive SOP may be present in the Elwha River system, but in small quantities not considered significant for the purposes of this study.

2.3.2 Iron Bound Phosphorus

The phosphorus–iron relationship has been established by many studies and is considered the traditional model for P release and immobilization (Kalff 2002 p. 247-249). Andisols, like those in the Elwha area (Wilson et al. 1996) have a high affinity for P. Phosphorus reacts with aluminum or Fe minerals to form Al or Fe phosphates, which have varying degrees of solubility (Negrin et al. 1998). The sediment entering Lake Mills will likely have similar andic characteristics. Soluble reactive phosphorus, in the water column or sediment porewater, adsorbs onto the Fe complex. Equation 1 is an expression of immobilization of P to form Fe~P, and the reverse reaction to release P:

Equation 1: $FeOOH + H_2PO_4^- \Leftrightarrow Fe(O\text{-}HPO_4) + OH^-$ (Golterman 2004, p. 57).

Pulatsu and Topcu (2009) report that phosphate chemistry in sediments and porewater is related to Fe concentrations, and elevated pH levels release P from Fe(III) hydroxides. This is due to the increased concentration of OH^- in solution, which replace phosphate in the Fe~P complex. The released P will not re-adsorb until the pH has decreased (Boström et al. 1982). The oxygen conditions will also affect Fe~P solubility. Negative/low redox potential conditions will dissolve the Fe~P complex to form soluble Fe(II), releasing P (Gunnars and Blomqvist 1997).

Under marine conditions sulfur also plays an important role in the Fe~P relationship (Gunnars and Blomqvist 1997). A supply of sulfide in sediments will bind a large portion of Fe as Fe sulfides, a phenomenon that may or may not occur in freshwater systems. Mitchell and Baldwin (1998) hypothesize that this may happen because of the presence of sulfate-reducing bacteria. The bacteria reduce sulfate to sulfide, which in turn reduces Fe(III) to Fe(II), releasing P and producing FeS (Mitchell and Baldwin 1998). Sulfate reducing bacteria can withstand drying conditions and are resistant to cell death due to limited water availability, indicating that that the bacteria an endure wetting and drying spells (Baldwin et al. 2000). Baldwin et al. (2000) found that after the addition of a C source and sulfate, more P was released, indicating a relationship between P, sulfate, C and probably Fe, probably as a result of sulfate reducing bacteria.

2.3.4 Calcium Bound Phosphorus

The other major form of P in sediments is Ca-bound P. This form depends on the concentration of Ca in the incoming and *in situ* sediment. Ca bound phosphate (Ca~P) occurs in two main forms, hydroxyapatite ($Ca_5(PO_4)_3$*OH) and tricalcium phosphate ($Ca_3(PO_4)_2$).

Calcium-bound P concentrations are heavily dependent on pH values, because acidic sediments will tend to dissolve the Ca~P complexes (Christophoridis and Fytianos 2006). Golterman (2001) discusses one of the earlier researchers in the biogeochemistry field, Clifford H. Mortimer. Mortimer (in Golterman 2001) suggested that anoxic conditions would cause dissolution of P from the Ca molecule. This is due to a lower pH under anoxic conditions and will dissolve the Ca (Golterman 2001). Golterman (1998) theorizes that incoming P will first adsorb onto Fe. When all the available Fe has P bound to it, excess P will form apatite with Ca, depending on the concentrations of Ca. Two types of Ca can be used to form apatite, either soluble Ca^{2+} or through surface adsorption of P onto $CaCO_3$ (Golterman 1998). Golterman also shows some evidence that the amount of Ca in solution could influence the immobilization of P through the binding of P to Fe minerals. Phosphorus immobilization will fluctuate between Fe and Ca depending on Fe, P and Ca concentrations.

2.3.5 Particulate Organic Phosphorus

Golterman (1998) reports that "There is no published evidence of a release [to the water column] of organic P by sediments." He suggests that the only relevant forms of labile P are from Ca and Fe-bound P. This is likely with low concentrations of organic matter or heavily decomposed organic matter leaving only humic acids (Christophoridis and Fytianos 2006). The Elwha River is oligotrophic and does not have large amounts of organic matter available to transfer P to the water column (Munn et al. 1999), indicating low concentrations of particulate and soluble organic P. Caraco et al. (1990) state that the organic matter in fresh-water systems could be highly depleted compared to marine systems. Low organic P transfer to the water column could also be due to high levels of immobilization in fresh-water

sediments via “P sorption, mineral formation and biotic uptake” compared to marine sediment systems (Caraco et al. 1990).

2.4 Phosphorus Release and Immobilization in Sediments

The SRP, Ca~P, Fe~P, OP and SOP are the main forms of P in the reservoir/lake system. Phosphorus is transformed from one form to another according to the processes in Fig. 2. Release of P is the disassociation of P from the solid Ca, Fe or organic complex to yield SRP. Immobilization of SRP is its binding to the surface or interior of a solid, usually Ca or Fe complexes, where it becomes unavailable for plant growth. Following release into porewater, SRP can diffuse into the water column or change between forms of P depending on the environmental conditions (Fig. 2). Phosphorus can be taken up by microbes or plants, released as SRP, adsorbed onto aggregate minerals and then deposited in the sediment (Boström et al. 1982) (See Figure 1 for a conceptual model of P dynamics in the ecosystem).

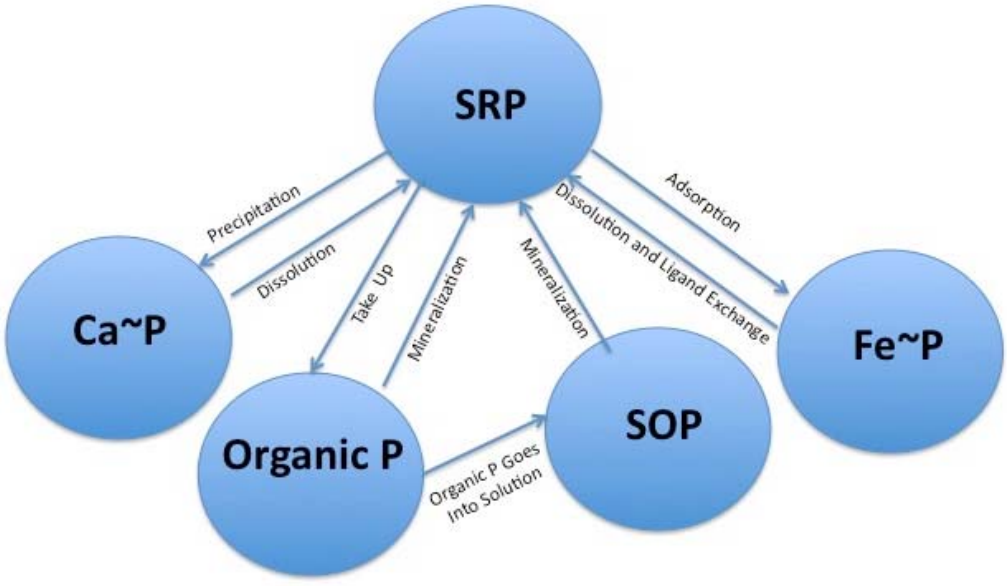

Figure 2. Processes connecting phosphorus in porewater and sediments. See Table 1 for descriptions of forms.

2.4.1 pH Influences on P Release and Immobilization

The pH of the sediments and water column will influence P release or sorption. The pH is influenced by primary productivity in the photoactive region of lakes. This usually occurs in shallow, productive lakes and may or may not be applicable to the Elwha system because of its low productivity. Also, most release of P is independent of pH as long as the pH is within the normal range expected in sediments: neutral to slightly alkaline. The pH outside of that range has been shown to affect Fe, aluminum, and Ca bound phosphorus (Boström et al. 1982). Elevated pH has been shown to release P from Fe~P compounds, and since Fe and P are closely related, a change in pH will affect P dynamics in sediments (Pulatsu and Topcu 2009). A lower pH will increase Fe binding of P. The ratio of SRP to Fe(III)-hydroxide in the porewater of the sediments also becomes important; low ratios of P:Fe will cause higher levels of desorption with increasing pH (Boström et al. 1982). Christophoridis and Fytianos (2006) suggest that the mechanism for P release at high pH is due to ligand exchange: phosphate ions are exchanged for hydroxyl ions, releasing P. If the pH lowers, P can be re-adsorbed to Fe compounds. Boström et al. (1982) assume that aluminum will react in a similar fashion to the Fe. Calcium-bound P is also influenced by pH. High pH conditions will cause P release; however, with high concentrations of Ca, P will be precipitated with the Ca, producing hydroxyapatite or Ca phosphate (Boström et al. 1982). Strong acids will dissolve Ca-bound P (Boström et al. 1988).

2.4.2 Redox Influences on P Release and Immobilization

The redox potential (Eh) of the sediments influences the release and immobilization of P in many different ways. When discussing the P cycle, Eh is one of the foundations of P release and sorption. This is due to the huge influence Eh has on sediment-P interactions. The

redox potential (Eh) is a measure of the intensity of the oxidizing and reducing conditions within a system. A positive Eh is oxidizing, while a negative Eh is reducing. A system will have changing Eh, primarily through aerobic microbial activity and respiration and thus oxygen concentrations (Kalff 2002, p. 239).

When organic matter settles to the lake bottom, microbes decompose the organic matter and with increasing concentrations of organic matter, oxygen use/consumption increases. The decomposition of organic matter at the bottom of the lake will create an anoxic layer of water and sediments. Under anaerobic conditions, released P stays in the water column due to the low amounts of microbial take up. Oxygen concentrations also change in the profile of the sediment. If the overlying water is oxic, the top few centimeters of sediment will also be oxic. Below two centimeters anoxic conditions predominate (Boström et al. 1982).

Lower Eh values dissolve the Fe-P complex, releasing P. This release is dependent on the Fe to total P ratio, the redox value and the many compounds that are redox active including nitrates and sulfates. Those same active compounds can also create a redox barrier between the sediment and water. A positive redox barrier will prevent the release of P by binding any SRP that would otherwise diffuse from the sediments (Christophoridis and Fytianos 2006).

2.4.3 Temperature Influences on P Release and Immobilization

Temperature increases influence chemical and biological factors in sediments and thus P release and immobilization. Boström et al. (1982) state that the major factors influencing P release are biological and chemical processes that are temperature dependent. Bacteria will increase in activity with increasing temperature to a certain point. Some studies suggest that under sufficiently warm temperatures, greater than 17 degrees Celsius, P diffusion into the

water column occurs equally under anaerobic and aerobic circumstances. This could be due to the breakdown of the oxic layer for diffusion to occur to the water column. The breakdown of the oxic layer occurs when microbial activity respires all the oxygen available, creating micro anaerobic conditions even under general aerobic conditions (Boström et al. 1982).

2.4.4 Biological Factors Associated with P Release and Immobilization

Biological activity can produce P-containing organic matter that is held in sediments as humic and non-humic organic materials. Biological activity can also decompose the P-containing organic matter to release the P. The mineralization of P is a result of bacteria breaking down organic P. Bioturbation or mixing can also increase the amount of P released by disturbing barriers to the water-sediment interface (Christophoridis and Fytianos 2006). Caraco et al. (1990) report that the decomposition of organic matter releases P, but the P could be taken up biologically. Microbial activity through the decomposition of organic matter can reduce the redox potential and therefore release P (Christophoridis and Fytianos 2006).

2.4.5 Nitrogen Influences on P Release

The presence of nitrates can influence P release or immobilization depending on which nitrate-influenced mechanism is the most prominent. Nitrate concentrations in sediments can increase the amount of P released by increasing the rate at which organic matter is decomposed (Boström et al. 1988). This mechanism depends on the quality of the organic matter available for decomposition. Nitrates buffer the redox potential through the reduction of nitrates instead of the reduction of Fe~P on surface sediments, limiting Fe~P release (Boström et al. 1988). Nitrate prevents the diffusion of SRP to the water column by being an

alternate electron acceptor instead of Fe(III), thus preventing the reduction of Fe and the release of P (Boström et al. 1982). When concentrations of nitrates are low, Fe can be used as an alternative electron acceptor by nitrate-reducing bacteria. The redox potential is lowered, Fe complexes dissolve, and P released from the complexes can increase dramatically (Boström et al. 1988).

2.4.6 Sulfur and Other Chemical Influences on P Release

Sulfate influences P release through reduction and binding of Fe. Concentrations of sulfates in sediments, under low oxygen conditions, can influence P release by reducing to sulfides and Fe(III) to Fe(II) then forming FeS from Fe~P, releasing P (Christophoridis and Fytianos 2006). This transformation is permanent and decreases the number of binding sites for P on Fe minerals (Boström et al 1982). Magnesium, and Mn influence P release through the redox potential indirectly (Christophoridis and Fytianos 2006).

2.4.7 Marine Water Influences on P Release

Marine and fresh waters influence the P cycle in different ways. A few sources report that marine waters are not influenced by the redox potential at all, meaning no low-redox facilitated P release (Hallberg et al. 1976; Holm 1978; Balzer 1980, 1984; Balzer et al. 1983; Sundby et al. 1986 as cited in Gunnars and Blomqvist 1997). Gunnars and Blomqvist are also skeptical of the Fe~P predominance and state that it is rather Mn binding P in marine waters or sulfate concentrations influencing P release. Gunnars and Blomqvist (1997) found that, while in both fresh- and salt-water, Mn showed redox-dependent behavior, it failed to interact with either P or Fe.

A study of fresh- and salt-water systems showed that these two systems are drastically different from each other in terms of P release and immobilization (Caraco et al. 1999). Fresh-water systems tend to be P limited, and the Caraco et al. (1999) study suggests this is due to the quality of incoming organic matter: “Decomposing organic matter in fresh-water systems are extremely depleted in P relative to that in salt-water systems and the low P release is a simple reflection of this depletion.” However, Caraco et al. (1999) do not discuss the relationship between P and salt-water ions. Jordan et al. (2008) discuss the effect a marine environment has on P release. They found an overall increase in P release, which they attributed to the presence of sulfides in marine water to dissolve the Fe~P complex. The organic P and SRP increased while Fe~P and total sediment P decreased (Jordan et al. 2008).

Beltman et al. (2000) report that the anions in the water, including chloride and sulfate anions, replace phosphate bound to metal complexes, causing release of P, available for plant growth. In that study, however, the increased release rate is counteracted with increased P uptake by plants and microbes. Boström et al. (1982) report that pH influences P release from the Fe~P complex. Under high pH conditions, P is substituted by OH^-. The P cannot be re-adsorbed until the pH has decreased, a likely mechanism for P release under marine conditions because of the excess of anions (Boström et al. 1982). Kalff (2002, p. 248) also discuss that under elevated pH P is released from the Fe~P complex and replaced with OH^-. However, increased anions in solution should make a difference compared to distilled water, increasing release of P.

2.4.8 Other Factors Influencing P Release and Immobilization

Other factors that influence P release or sorption are often physical factors of the reservoir and environment. The morphology of the lake influences the residency time of the body of water, which changes the equilibrium of P concentrations between the sediment and water column (Gächter and Wehrli 1998). The concentration of P that naturally occurs in the sediments and soils and history of pollution and trophic level of the lake will influence the forms of P and concentrations (Baldwin et al. 2000).

Particle size of the sediments entering and in the system can influence P release and binding. Selig (2003) notes that different P-forms can be associated with different particle-size classes. Huijun et al. (2010) found that specific forms of P were associated with different particle-size classes in the Yellow River downstream from the Xiaolangdi Reservoir. They found that the bioavailable, exchangeable, organic, authigenic, and refractory P fraction of P were associated with clays, very fine and fine silts. Detrital P was associated with medium to coarse silt fractions. Calcium bound P was found with all sizes of particles (Huijun et al. 2010). Particle size is also important for the ability for the sediments to be resuspended; resuspended, smaller particles have a large capacity to bind P (Selig 2003 and Huijun et al. 2010).

2.4.9 Diffusion/transport of SRP to water column

In order for phosphorus to diffuse from the sediment to the water column, it will often need to pass an oxic barrier. This barrier causes the oxic sediments to adsorb SRP onto Fe, becoming Fe~P (Boström et al. 1982). The oxic layer of sediments is caused by the oxic water overlying the sediments. However, if the water overlying sediments is anoxic then

diffusion happens if the concentration of SRP in the water column is less than the concentration in the porewater of the sediments. If there is an oxic layer, it needs to be broken up for diffusion to happen. This can happen in many ways: wind, ebullition, bioturbation, nitrate concentrations, organic matter concentrations, and microbial activity. Wind causes mixing to occur on surface sediments, which can release porewater to the water column. Ebullition occurs under anaerobic conditions, gases bubble up from the sediment, bringing along with them SRP. Bioturabtion acts the same way that ebullition and wind, the creatures mix up the sediments and release SRP to the water column (Boström et al. 1982). Nitrates change the redox potential of the oxic layer, either aiding release or delaying it (see Section 2.4.5). Microbes will also cause a decrease in redox potential if there is sufficient N, P and organic matter (see Section 2.4.4). Other methods of release to the water column are transport by rooted plants that take up SRP in the porewater of sediments and release it to the water column (Boström et al. 1982).

3.0 Methods

3.1 Collection Site

Of the two dammed reservoirs on the Elwha River, Lake Mills was chosen to sample because of the greater volume of sediment. Lake Mills is the reservoir created by the Glines Canyon Dam that was built between 1925 and 1927. The dam is at river kilometer 21.6 and is 64 m in height. Lake Mills has an area of 1.68 km^2 and stores 5.12 x 10^7 m^3 (Duda et al. 2008). Up stream from Lake Mills the water quality was tested for nutrient concentrations and the phosphorus and N concentrations are very low (as discussed in Munn et al. 1999). Additional tests done for metals, pesticides, volatile organic compounds and radionuclides were below detection limits. The same study found sufficiently low N and phosphorus concentrations that the Elwha River and its reservoirs are considered an oligotrophic system. The Elwha River has limited primary and secondary production (Munn et al. 1999).

3.2 Sample Collection

3.2.1 Lake Sample Collection

Sediment samples were collected on June 27-28, 2008 from four points in Lake Mills and four points on the Lake Mills Delta (Fig. 3). The lake sediments were collected between 7 and 9 m water depth with the help of personnel and equipment from Gravity Environmental, Seattle, WA. A Van Veen Power Grab attached to a boat was used to collect sediments to an approximate depth of 17 cm. After the grab was brought to the surface, sediments were put into a Ziploc 0.65 L plastic bag, which was inserted into a 2 L plastic bag that also contained sediments, thereby creating a sacrificial layer between the atmosphere and the inner, smaller bag as described by A. Tessier (Baldwin 1996a).

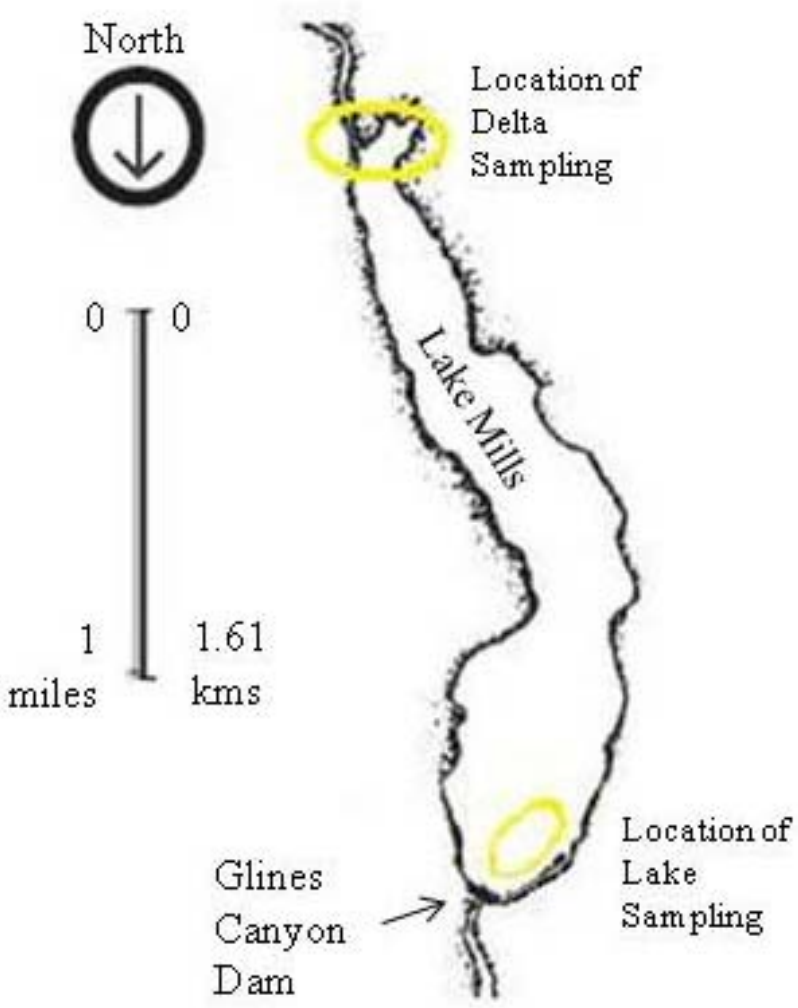

Figure 3. Map of Lake Mills system and location of sampling sites (Olympic National Park).

3.2.2 Delta Sediment Collection

Another four sediment samples were collected on the Lake Mills delta, a small island to the east of the main river. The delta samples were collected on a north-facing island. Two samples were collected near the waters edge and another two samples were collected a meter away from the water's edge. All four locations were exposed to air, and had high water content. The samples were inserted into plastic bags. They were bagged twice and no sacrificial layer was used.

3.3 Sediment Storage and Preparation for Analysis

The sediments were refrigerated within 36 hours after collection and refrigerated continuously thereafter. In preparation for general characterization, two subsamples were removed from each of the plastic bags in August 2008. The subsamples were placed in beakers to allow standing water to evaporate. Then they were placed on drying paper to air dry. After drying, the sediments were separated by sieves into >2 mm, 0.5-2 mm, and <0.5 mm fractions. All characterization analyses were performed on <0.5-mm fractions so the few >0.5 mm particles would not bias results. The remaining sediments were refrigerated in the plastic bags until the incubation and isotherm studies. No sieving was performed on the sediment samples for the incubation and isotherm studies.

3.4 Approaches to Evaluate Phosphorus Dynamics

The objectives of my study were to characterize P in Lake Mills sediments and determine factors that influence P dynamics. To accomplish these objectives, three types of assessments were carried out: phosphorus fractionation, phosphorus incubation under contrasting environmental conditions, and phosphorus isotherm.

3.4.1 Necessity of Choosing a Phosphorus Fractionation Scheme

The various forms of P in sediments are quantified through chemical extractions. Ideally, a chemical extraction would correspond to a specific phase of P in the sediment, but it is hard to prove that it does so. Methods have been developed over the last century to analyze different forms of P in soils and sediments. Initial methods dealt specifically with soil samples and were later adapted for use in sediments. These methods vary in complexity and reproducibility; however, Barbanti et al. (1994) state it well: "The best sequence [P fractionation procedure] to use should be chosen taking into account the peculiarities of each sequence and the contents of detrital apatite and organic matter of the sediments under study." My study prioritized fractionation schemes based on reproducibility and ease of procedure as the laboratory used was not set up for P analysis and all supplies and materials needed to be borrowed or purchased. The sediments had unknown amounts of detrital apatite and very low organic matter.

3.4.2 Different Procedures for Phosphorus Fractionation

There are two basic types of P fractionation: "The 'strong' ones using HCl-NaOH and the 'soft' ones using chelators such as nitrilo triacetic acid or EDTA," (Ruban et al. 1999b). The 'soft' Golterman method was first published in 1977 (Golterman 1982). This method is designed to prevent readsorption of P by the sediments. The Fe is extracted to prevent readsorption of P by the Fe complex. Golterman found that extracting with EDTA had similar recoveries to the strong acid extractions. However, Golterman admits that his method is cumbersome (Golterman 1982). Ruban et al. (1999a) found the Golterman procedure to extract specific compounds (ex. Fe~P), organic P, and provides information on the bioavailable fractions in sediments. The same paper lists the disadvantages of the Golterman

extraction as cumbersome, extractants interfere with measuring P, the solutions are complicated and the extractions sometimes have to be repeated.

Ruttenberg (1992) describes the 'soft' SEDEX method, which is used for the analysis of P in both marine and fresh water sediments. The SEDEX method has the advantage of being able to differentiate between authigentic (formed *in situ*) and detrital apatite (deposited apatite). After the extractant is made in contact with the sediment, the residue (extracted sediment) is washed to prevent readsorption (Ruttenberg, 1992). Ruban et al. (1999a) reported that the SEDEX method was impractical and that the butanol extraction is difficult to do properly. Barbanti et al. (1994) reported that the SEDEX method also had problems with readsorption despite the washing. The same study found that both the Golterman and SEDEX methods had problems in giving organic P values.

The other methods, the 'strong' methods for P analysis, include some variation of the following methods: Williams, Hieltjes-Lijklema, Psenner-Jensen-Thamdrup, and Fytianos-Kotzakioti. These methods usually use strong acids and bases to extract P from three different forms of P, four including total P.

The 'strong' procedures use some sort of combination of HCl, and NaOH for extractions, varying in concentration and extraction procedure. The disadvantages of most of these methods is the problem with readsorption and problems associating extracted P with form of P. Ruban et al. (1999a) found that the Hieltjes-Lijkema method dissolves both Fe-bound P and Al-bound P as well as organic P during a particular step in the procedure leading to a lack of correlation between the extraction and actual form of P. Ruban et al. (1999a) states that the Williams procedure allows for the readsorption of P onto $CaCO_3$. Both these

methods are simple, practical and inexpensive to execute (Ruban et al. 1999a). The Psenner-Jensen-Thamdrup and Fytianos-Kotzakioti procedures use similar chemical extractants but include bicarbonate-dithionite (BD) to extract Fe-bound P (Jensen and Thamdrup 1993, Fytianos and Kotzakioti 2005). The extraction for Fe-bound P using BD was part of the Williams procedure as well, but was later eliminated when it was found that the procedure worked just as well without it (Ruban et al. 1999a).

3.4.3 Selection of Procedure for Phosphorus Fractionation

The modified Williams procedure as outlined in Ruban et al. (1999a) was used in this study to analyze the sediments for Fe-bound P, Ca-bound P, organic P, total P and inorganic P (included in the appendix). The Williams procedure was initially outlined and then modified in the following papers: Williams et al. 1970, and Williams et al. 1980. This procedure was chosen because of its ability to be reproduced, simplicity, inexpensiveness and the comparative study performed by Ruban et al. (1999). Ruban et al. (1999a) took four extraction methods and sent them out to many different laboratories across Europe to analyze the same material. They found that the Williams procedure was the most easily reproduced and accurate method. The disadvantages of the Williams procedure are, as mentioned above, the readsorption of P onto $CaCO_3$ and the tendency to underestimate organic P due to losses during ashing. Underestimation of organic P is unlikely because of the low concentrations of organic matter.

3.4.4 Incubation under Multiple Environmental Conditions

The incubation study was designed to improve understanding of P release from sediments under differing environmental conditions. The method that was eventually used was

developed through trial and error and through the research in the literature that had conducted similar studies. Similar studies done in Australia by Baldwin et al. (2000) analyzed drying in eutrophic reservoirs and wetlands; and the drying's effect on the sediment's ability to retain and release P. The difference between those systems and the Elwha is the amount of nutrients coming into the system, but the idea to try to determine release of P through an incubation was very similar.

The incubation was designed to test how water quality, atmosphere, sediment type and incubation time influenced P release. This was to mimic what might happen after the dams are removed. The water types included fresh and salt water, because sediments could remain in the freshwater river or be transported to the marine Strait of Juan de Fuca.

The atmosphere types were air (pressurized air, atmosphere composition of elements) and N gas. The atmosphere as a treatment is of importance because of the effects of low oxygen levels on P release. Many studies dating back to Mortimer's studies in the 1940s have found that more P is released under anoxic conditions (Baldwin 1996a, Baldwin et al. 2000, Mitchell and Baldwin 1998, Pulatsu and Topcu 2009, Chambers et al. 1995, Gunnars and Blomqvist 1997, Christophoridis and Fytianos 2006, Gächter and Wehrli 1998, Nurnberg 1984, Nurnberg 1987, among many others). The oxygen concentration controls the sorption of P onto Fe complexes, as discussed in earlier sections. This relationship between oxygen and Fe~P is explored with treatments of N gas or air atmospheres in order to discover the effect of atmosphere type would influence P release from Elwha sediments.

The sediment types included coarse sediments from the delta and fine sediments from the bottom of Lake Mills. Huijun et al. (2010), as mentioned above, found particle size can

influence the reactivity of sediments and thus P. The differences in particle size between these two sediments were studied to see how the different sizes would influence P release. The time treatments included four-hour and two-week incubations. This allowed a comparison of short and long-term exposure to the incubation conditions.

3.4.5 Isotherm Study

An isotherm study was designed for the Elwha sediments to see how much P the sediments could adsorb. Baldwin (1996a) did a similar study involving sediments in an eutrophic reservoir. The Baldwin study was interested in how P dynamics changed with changing environmental conditions like wetting, drying and rewetting. The Elwha isotherm study was similar to the incubation study, but the treatments were different concentrations of P under fresh water, N atmosphere conditions. The ability for Elwha sediments to retain large quantities of P is derived from andic soils.

3.5 Physical Characterization

Air-dried <0.5mm fractions were ashed at 450° C for three hours to remove organic matter that might aggregate the sediments. A scoop of sediment was put into 30 ml of deionized water, then a scoop of Calgon, sodium hexametaphosphate was added as a dispersant. The mixture was then measured on the Malvern Mastersizer Particle Analyzer (Malvern Instruments Ltd, Worcestershire, United Kingdom). Because the delta sediments were extremely course, they were re-sieved at 0.3 mm and reanalyzed; the values were not substantially different from the initial results. The larger grained sediments tended to fall out of solution, which would have prevented their measurement, biasing the results. Several runs

of the same sediment were analyzed to obtain the best estimate of the particle size distribution for that sample.

3.6 Chemical Characterization

The <0.5 mm fractions were dried at 105° C over night and cooled in a desiccator before analysis on a Thermo Electron NC Soil Analyzer Flash EA 1112 Series (Thermo Electron Corporation, Milan, Italy). A known mass of material of ~200 mg was put into a tin capsule and the capsule was compressed to remove any air prior to inserting into the instrument with an autosampler. The standard curve was made from Soil Reference Material NC det. (P/N 338 40025, Thermo Electron Corporation, Milan, Italy). The standard had 0.186% N and 1.70% C. The mass of C in the standard curve ranged from 0.200 mg C (expected value: 0.200 mg C) to 0.979 mg C (expected value: 0.945 mg C). The C calibration curve had an R^2 of 0.997. The mass of N in the standard curve ranged from 0.0219 mg N (expected value: 0.0220 mg N) to 0.107 mg (expected value: 0.104 mg N). The N calibration curve had an R^2 of 0.999. The quality control was a within-lab QC soil sample and had 0.242% N and 2.97% C. The observed values for the quality control sample were 0.233% N and 2.93% C.

Analysis of amorphous Fe on air-dried <0.5mm fractions followed the procedure of Chao and Zhou (1983). A 0.175 M ammonium oxalate–0.100 M oxalic acid extracting solution was made in Nanopure water. A known mass of material of ~100 mg was weighed into a centrifuge tube, then 25 ml of the extracting solution was added to the tube. The centrifuge tube was capped and put on a shaker table in the dark for four hours (Chao and Zhou 1983). After shaking, the tubes were centrifuged for five minutes and then a 10 ml aliquot of each extraction was separated from the sediment and refrigerated until analysis on the flame atomic absorption spectrometer (FAAS). The FAAS used was the Varian SpectrAA 220FS

w/ SPS-5 with SIPS auto sampling and the Varian Fe lamp (Varian, Inc., Palo Alto, California, USA). The samples were brought to room temperature and transferred to sample tubes for the autoanalyzer on the FAAS to run the samples. An air/acetylene mixture was used to volatilize the samples (Varian, Inc. 1989. pp 23). A standard curve was generated using the auto-sampler and a quality control (30 ppm Fe) was sampled every 5^{th} sample. The standard used to generate the standard curve was 30 ppm Fe. The average measured value of the quality control samples was 27.1ppm Fe, and the actual value was 30 ppm Fe.

Several forms of P were extracted from air-dried <0.5mm fractions using the modified William's protocol (Ruban et al. 1999a). Phosphorus was extracted sequentially, first with NaOH to yield the fraction called NaOH-P. The residue from that extraction was rinsed with NaCl and then extracted with HCl, yielding a fraction called HCl-P. On a second subsample, phosphorus was extracted sequentially, first with HCl, then the residue was rinsed and ashed, then extracted with HCl as well, to yield fractions called inorganic and organic, respectively. The TP sediment sample was ashed and then extracted with HCl. All extraction solutions were neutralized with NaOH, using phenolphthalein as an indicator. Under neutralized conditions an accurate standard curve could be constructed. The solutions were analyzed at 882 nm on the Spectronic 21D (Murphy and Riley 1962). Before all solutions were measured, the instrument was zeroed out on the matrix blank. After the solutions were measured another matrix blank was measured to check for instrument drift. The blanks ranged from 2% to 10% of the average values, giving about 2% to 10% error, including contamination. There was very little instrument drift, between a 0.1 to 0.01 off from the initial blank reading. The absorbance was recorded and converted to the proper units using a standard curve made in the matrix of the neutralized extraction solution. The standard curves

were performed for each matrix and all values fell within the standard curve after dilution of some samples. The analysis for TP, Ca~P and Fe~P had to be diluted to be measured with the spectrometer and fit with a standard curve. Organic P was in the range for the standard curve and the instrument. All chemical and physical characterizations were performed on two subsamples of each of the four sub-locations of each location (lake or delta), for a total of 16 samples analyzed.

3.7 Incubation

The incubation was a four-factor ANOVA experimental design, with two levels for each factor: sediment type (lake or delta), water type (fresh or salt), atmosphere (air or N), and incubation time (4 or 300 hours). There were three replicate incubation tubes for each combination of levels. The incubations were carried out in 50-ml centrifuge tubes. Each tube was color coded and labeled with a number to ensure accuracy of the application of the treatments. The tubes were administered the water type and atmosphere treatments in random order to prevent bias. However, to ease setting up the study, delta sample was processed first, followed by lake sample. Two sediment samples were chosen for the incubation, one from the lake and one from the delta. These sediments are midrange in all their measured characteristics. Prior to the incubation, these sediments were refrigerated in the sample collection bags. No sieving was performed on these sediment samples for the incubation or isotherm studies.

The fresh water treatment included only Nanopure water. The salt water was prepared in degassed Nanopure water with the addition of 1470 mg/L of calcium chloride, 4000 mg/L of sodium sulfate, 10780 mg/L of magnesium chloride and 23500 mg/L of sodium chloride

(Eaton et al. 1995). The water was degassed for an hour by putting an N gas line into the carboy.

To administer the treatments, a scoop of sediment was put into a previously weighed 50-ml centrifuge tube, weighed again, water added to retain an ~10 ml headspace, and weighed again. This procedure minimized potential water loss and contamination. The ratio of water to dried-mass equivalent of sediment averaged 9 ml water: 1 g sediment. After the water was added, the headspace was flushed with compressed air or N for between 10 and 20 seconds, then the tube was capped. The tube was shaken on a shaker table for 4 hr or 300 hr in the dark at room temperature. For the 300 hr incubation period, every 24 hours the headspace was flushed and replaced with the appropriate gas. Following incubation, the tube was centrifuged for ten minutes and the supernatant removed.

The supernatant was filtered through a Pall Gelman magnetic vacuum filter apparatus using 0.45-µm Millipore mixed cellulose membrane filter. The filter apparatus was rinsed before and after each supernatant was filtered. The filtrates from the 4-hour treatment were frozen for two weeks. The filtrates from the 300-hour treatment were frozen over night. The filtrates were thawed, shaken and analyzed for soluble reactive phosphorus using the Alpkem FS3000 autoanalyzer (Reference: Standard Methods for Examination of Water and Wasterwater, 20th Ed., APHA Methods Orthophosphate 4500-P G). The saltwater samples were analyzed using salt water in the carrier and wash water, while the fresh water samples were analyzed with only Nanopure water. The sediments were converted to oven-dried masses after measuring the wet mass of the same sediments and then oven drying the sediments and weighing them again. This gave the wet to dry mass ratio and was used for the conversion in the incubation and isotherm studies.

3.8 Sediment Isotherm

The freshwater–air–300-h incubations were repeated, beginning with solutions containing 50, 100, or 1000 mg PO_4-P/L. Each concentration was run in triplicate for each sediment sample. Equation 2 was used to calculate immobilized P:

Equation 2: Immobilized P = ((I-F)*V)/M

where I is the initial concentration of P in µg P per liter, F is the final concentration of phosphorus in micrograms P per liter, V is the volume in liters of the solution and M is the mass in kilograms of the sediment. The solutions were analyzed in the same manner as the incubation study.

3.9 Quality Control for Isotherm and Incubation Study

A 15 µg P/L spike and blank were included for each atmosphere x time combination of each type of water, with an additional spike and blank for the isotherm, which used freshwater. The five freshwater spikes averaged 100% of the expected value and the CV was 2.7%. The five freshwater blanks ranged from 1.7 to 3.7 µg P/L. The four saltwater spikes averaged 87% of the expected value and the CV was 3.1%. The four saltwater blanks ranged from 0.2 to 3.1 µg P/L.

3.10 Statistical Analysis

All data were converted to oven-dried mass basis based on analysis of water content of the sediments. To better address the assumption of homogeneity of variances, many of the physical and chemical characteristics were $\log_{10}$-transformed. All characterization variables were analyzed by one-way ANOVA by sediment type (lake versus delta), with an alpha = 0.05. The incubation data were $\log_{10}$-transformed after adding a constant of 5 to address the

assumption of homogeneity of variances. The transformed incubation data were analyzed with a four-way ANOVA (sediment type, atmosphere, water type, and time; all fixed factors), and a Tukey multiple comparison test, with an alpha = 0.05. When transformations were made, back-transformed means and 95% CIs are presented.

4.0 Results

4.1 Characterization Study

Coarse fragments (>2 mm) averaged 0.03% of total delta sediments, and there were no coarse fragments in the lake sediments. Delta sediments had 12 times more sand than lake sediments, and much less silt and clay (Table 2). The mean particle size of the delta sediments was 24 times bigger than the mean particle size of the lake.

Delta sediments had a third as much amorphous Fe as the lake sediments; however, the amount of Fe bound phosphorus in the delta sediments was two-thirds that of the lake sediments (Table 3). Delta sediments had lower values in all phosphorus fractions. The delta sediments had four-fifths the amount of Ca bound phosphorus as the lake sediments, and three-fifths as much organic phosphorus.

The delta sediments had significantly less C and N (1/3 as much and 2/3 respectively) compared to the lake sediments (Table 4). However, the delta sediments had half the C to N and C to organic phosphorus ratios as the lake sediments. The N to organic phosphorus ratio for both the lake and delta sediments was about the same.

Table 2. Particle size distribution [mean (95% CI)] of delta and lake sediments from Lake Mills. n = 4 locations per sediment type.

Sediment	Sand†		Silt	Clay	Mean particle size‡
	——— % of <2 mm ———				µm
	Coarse Sand (0.5-2mm)	Fine Sand (0.05-0.5mm)			
Delta	3.9	98.2	1.8	0.0	282.9
	(-0.8-8.5)	(96.7-99.5)	(0.4-3.0)	(-0.02–0.09)	(241.4-331.4)
Lake	0.1	7.9	85.3	6.2	11.6
	(0.0-0.1)	(7.2-8.5)	(83.6-86.9)	(5.6-6.7)	(10.3-13.2)
P*					<0.001

† Sand = 50-200 µm, silt = 2-50 µm, clay = <2 µm; as per "Soil Properties" (2010).

‡ Geometric mean and 95% CI back-transformed from log-transformation.

* P value from 2-sample test

Table 3. Amorphous Fe and P fractions [mean (95% CI)] of delta and lake sediments from Lake. n = 4 locations per sediment type.

Sediment	Amorphous Fe‡	Fe-bound P‡	Ca-bound P‡	Organic P‡	Total P‡
	——— mg / kg oven dried sediment ———				
Delta	624	83	260	52	234
	(581–670)	(76–90)	(240–281)	(42-64)	(152–360)
Lake	1855	102	319	83	313
	(1748–1969)	(85–123)	(283–359)	(77–91)	(245399)
P†	<0.001	0.015	0.004	0.001	0.11

† P value from 2-sample test

‡ Geometric mean and 95% CI back-transformed from log-transformation.

Table 4. Carbon, N and elemental ratios [mean (95% CI)] of delta and lake sediments from Lake. n = 4 locations per sediment type.

Sediment	C‡	N‡	C/N	C/organic P	N/organic P
	%	%			
Delta	0.21	0.046	4.46	39.8	8.9
	(0.18-0.23)	(0.040-0.052)	(4.4–4.6)	(38.0–41.5)	(7.4–9.9)
Lake	0.63	0.071	8.9	75.6	8.7
	(0.57–0.68)	(0.062–0.081)	(8.2–10.3)	(62.1–82.2)	(7.4–9.9)
P†	<0.001	<0.001			

† P value from 2-sample test

‡ Geometric mean and 95% CI back-transformed from log-transformation.

4.2 Incubation Study

The incubation study showed the complex nature of phosphorus release under the incubation conditions. The four-factor ANOVA results showed the following significant main effects and interactions (P values in parentheses): time (<0.001), water type (<0.001), sediment (0.036), time*water type (<0.001), sediment type*time*water type (0.001). However, atmosphere type had a very high P-value of 0.308, indicating that the atmosphere type did not influence the amount of phosphorus being released. Figure 4 shows the lack of difference between N and air atmosphere on P release. The atmosphere types release P equally under changing conditions as shown by the points following the 1:1 line on the figure. Based on this lack of effect, atmosphere was removed as a factor from future analysis.

For delta sediments in both freshwater and saltwater, the amount of P released was 2 to 3 times larger at the longer incubation period than at the shorter period (Fig. 5). For lake sediments in saltwater, P released was 5 times greater at the longer period than the shorter period, but no incubation-period effect was observed in freshwater.

The amount of P released from delta sediments was 2 times greater in freshwater than in saltwater at both short and long incubation periods. In contrast, for the lake sediments, P release was an order of magnitude larger in freshwater at the shorter incubation period, but no difference between fresh- and saltwater was observed at the longer incubation period.

Delta sediments released 2 times as much P as lake sediments in saltwater at the short incubation period. No other differences between delta and lake sediments were observed.

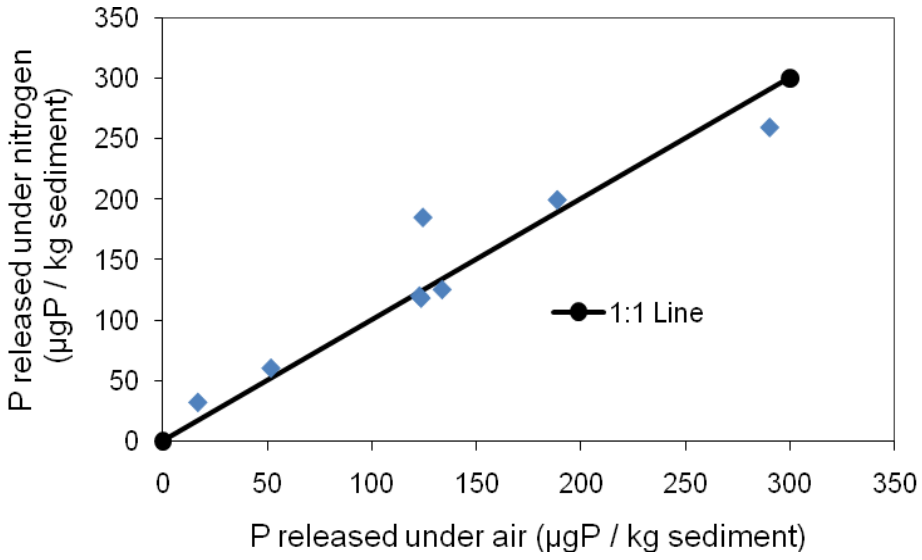

Figure 4. Comparison of P released under N and air atmospheres. Each point is the back-transformed mean phosphorus released under air and N for a particular treatment combination of sediment (lake and delta), water types (fresh and salt), and time (4 or 300 hours).

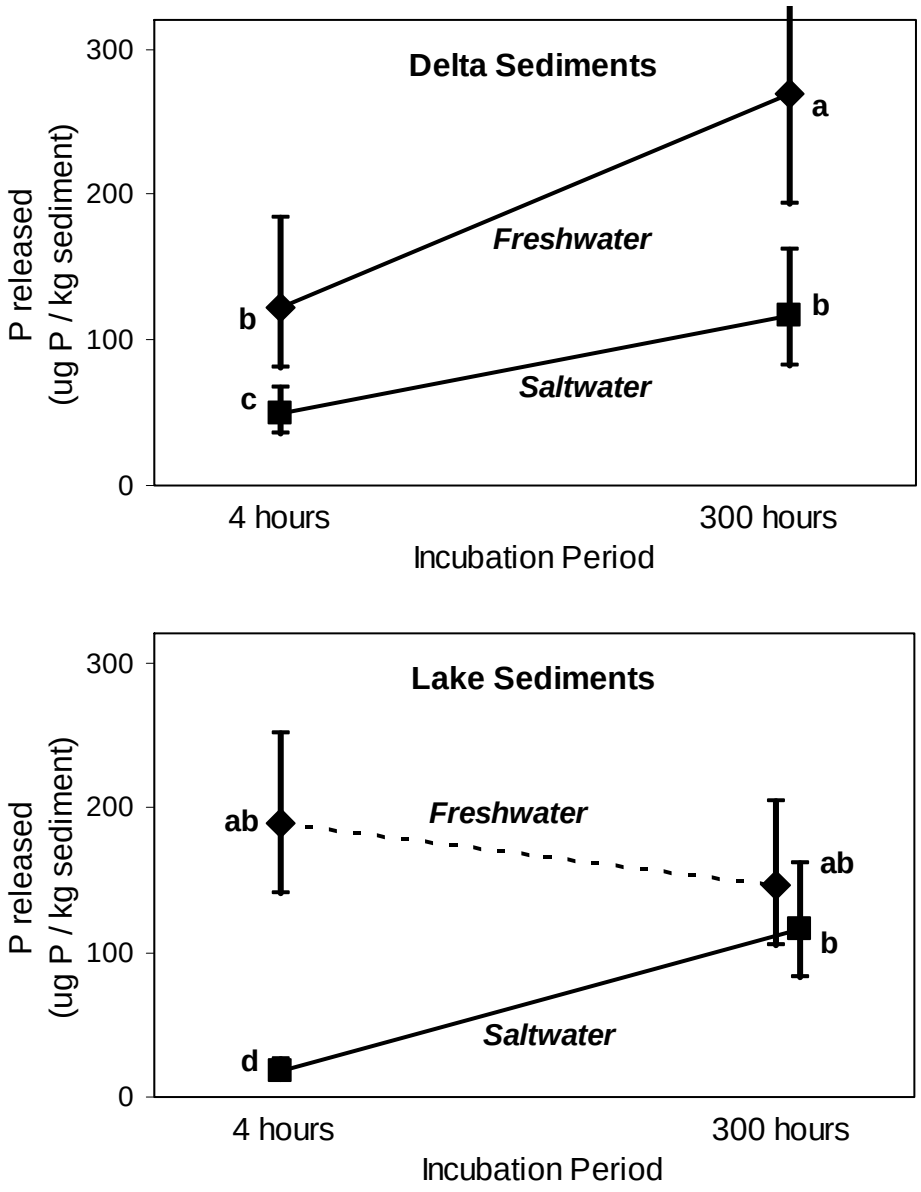

Figure 5. Phosphorus release from delta and lake sediments incubated in fresh- and salt-water for short and long incubation periods. Statistical analyses were carried out on log(P+5) transformed data. Values presented are back-transformed means ± 95% CIs of the log-transformed data. Means not followed by a same letter are different at $P<0.05$ (Tukey test of log-transformed data carried out across all means). n=4 to 8 per mean. A solid line between means indicates a significant difference; a dotted line indicates no difference was observed. ***

4.3 Isotherm

The isotherm results indicated the lake sediments had an extremely high capacity to immobilize P (Fig. 6). The lake sediments maintained the P concentration in water at 11 µg P/L even after immobilizing 1,000,000 µg P/kg of sediment. The delta sediments maintained the P concentration in water at 20 µg P/L up to 100,000 µg immobilized P/kg, then P concentration in water increased to 51 µg P/L at 1,000,000 µg immobilized P/kg of sediment. The lake sediments on average kept about half as much phosphorus in solution as the delta sediments.

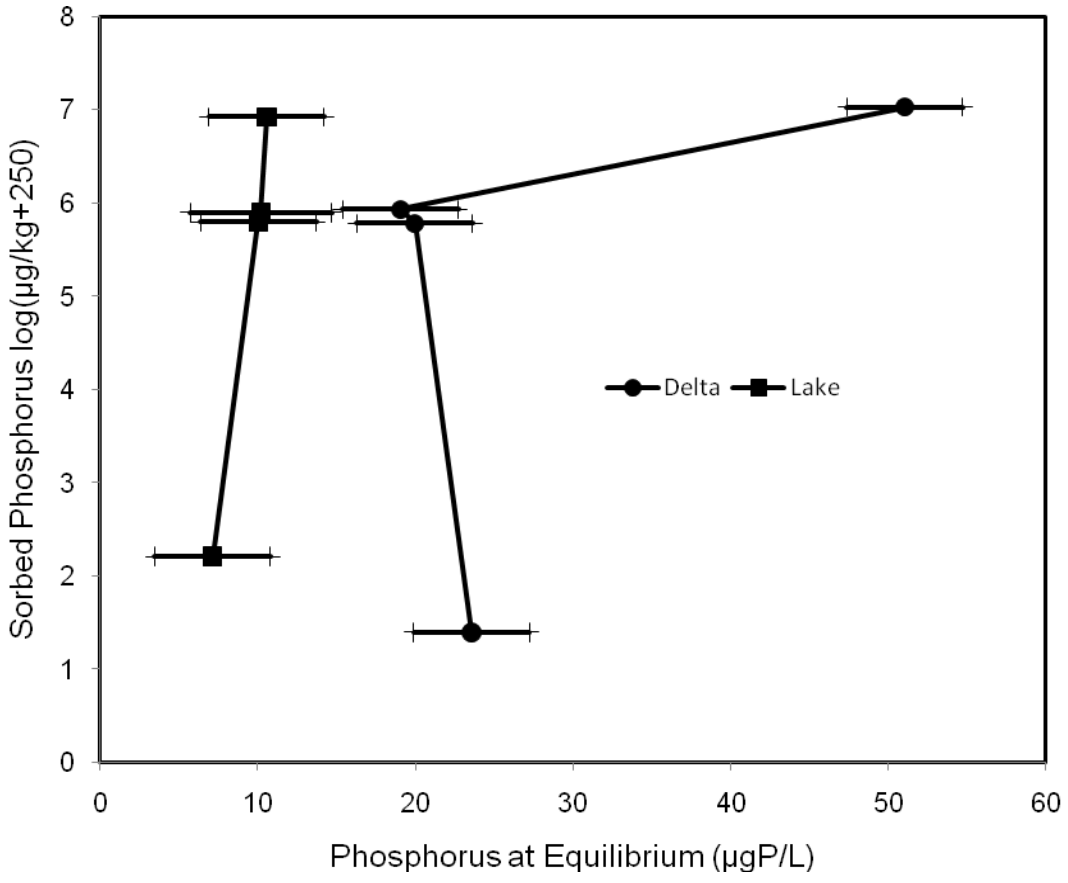

Figure 6. The isotherm of sediments and phosphorus shown as the amount of sorbed phosphorus vs. phosphorus in water at equilibrium.

5.0 Discussion

5.1 Characterization Study

The characterization study provides us with information about the different forms of P in the sediments and the difference between the two sediment types. The forms of P and the changing environmental conditions relate to P release and immobilization. Different fractions of P will release under different conditions, so the dominate fractions of P will help managers understand under what conditions P release can be expected.

The results from four papers that used the same extraction method as my study are displayed in Table 5 and Fig. 7. Pardo et al. (2003a) analyzed sediments to determine the partitioning of P in sediments. The sediment samples were oxic, lake or reservoir samples from the Barcelona area. The sediments were classified as "Organic rich sediments, calcareous sediments, and sediments with high Fe content and medium to low Ca and organic matter contents," (Pardo et al. 2003a). Within each class there was a wide range of concentrations (Table 5). Ruban et al. (1999b) report the relative distribution of P in the Bort-Les-Orgues Reservoir in Table 5. The Bort-Les-Orgues is an area of high agricultural use with effluents that are rarely treated; the agricultural runoff is the main source of nutrients for the Bort-Les-Orgues (Ruban and Demare 1998).

The relative distribution of P is remarkably similar in the lake and delta Elwha sediments (Table 5). It follows the order Ca~P > Fe~P > organic P. This is the same order as the average of the published studies (Table 5). In contrast, Fe~P was the dominant P fraction in Bort-Les-Orgues Reservoir sediments (Table 5, Ruban et al. 1999b), which had been influenced by agricultural runoff. The Elwha sediment P concentrations were much lower

than literature averages (Fig. 7). This is likely the result of low organic inputs and potentially P-limited geology of the area.

Table 5. Concentration of P (mg P/kg) from the literature and Elwha Sediments. Pardo et al. 2003a are sediments from oxic lakes and a reservoir. Pardo et al. 2003b sediments are similar to Pardo et al. 2003a and come from the same region in Barcelona. Ruban et al. 1999a are freshwater sediments, and unfortunately, not more information was provided. Ruban et al. 1999b are freshwater sediments from the Bort-Les-Orgues Reservoir, the reservoir is highly influenced by agricultural runoff.

Source		Fe~P	Ca~P	OP
			mg P/kg sediment	
Pardo et al. 2003a			Organic Rich Sediments	
	Minimum	1029	319	332
	Maximum	2231	4929	906
			Calcareous Sediments	
	Minimum	93	293	95
	Maximum	1007	2147	266
			Sediments with high Fe content and medium to low Ca and organic matter contents	
	Minimum	92	263	82
	Maximum	1392	1733	440
Pardo et al. 2003b		580	505	205
Ruban et al. 1999a			First Interlaboratory Trial	
	Minimum	92	352	154
	Maximum	165	338	180
			Second Interlaboratory Trial	
	Minimum	88	328	106
	Maximum	2055	615	886
Ruban et al. 1999b		1590	410	650
	Literature Mean	868	1019	359
	Literature Coefficient of Variation	93%	135%	84%
Cavaliere (present study)				
	Elwha Delta Sediments	83	260	52
	Elwha Lake Sediments	102	319	83

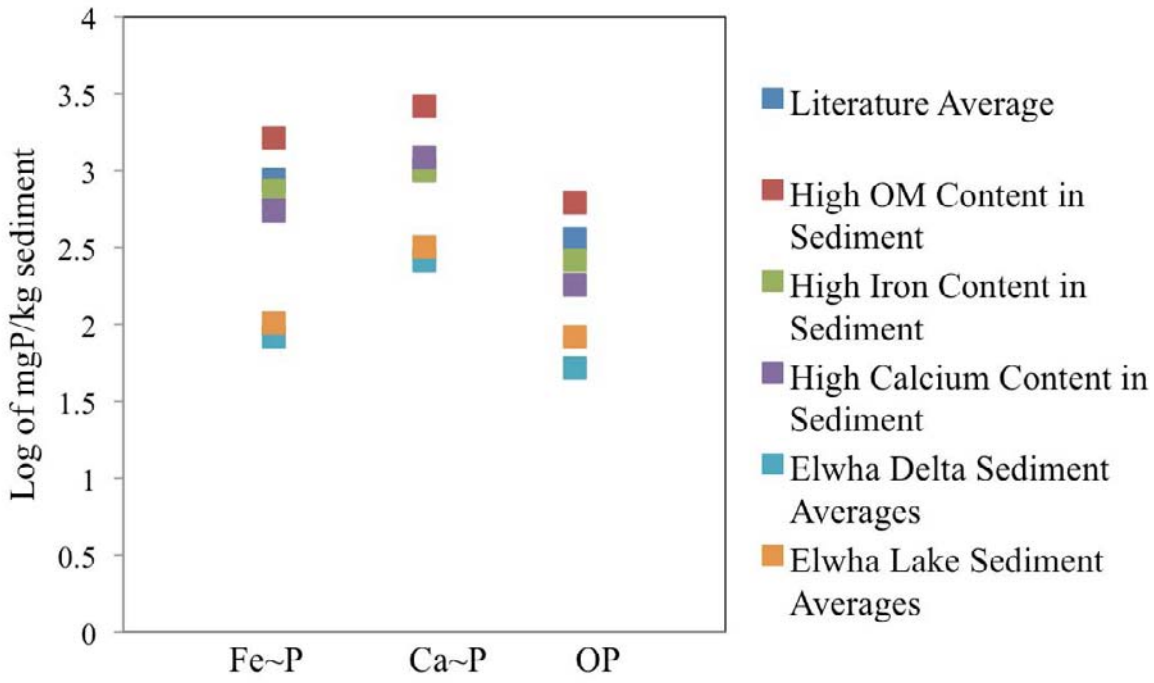

Figure 7. Concentrations of P from Pardo et al. 2003 a, b; Ruban et al. 1999 a, b; Elwha Delta and Lake sediments.

In spite of low amounts of Fe~P, the amorphous Fe (Table 3) indicates high levels of Fe available for P binding in Elwha sediments. Baldwin (1996a) studied an Australian reservoir that experienced repeated blooms of blue-green algae, suggesting sufficient to excess concentrations of nutrients. Baldwin (1996a) reported values much lower values for amorphous Fe, between 2.9 and 9.4 mg/kg, almost 100 times less than in the Elwha sediments. Baldwin et al. (2000) studied a mesotrophic oxbow lake in Australia (Baldwin 1996b). The lake sediments had between 100 and 1500 mg/kg of Fe released after prolonged incubation; that same fraction of Fe can be assumed to be amorphous Fe. The Baldwin et al. (2000) values were much closer to those of the Elwha sediments. This indicates that the amount of Fe found in the Elwha sediments is in a range found in other places and studies.

Sediments exposed to agricultural runoff will have high inputs due to fertilizers and manure, leading to large inputs of nutrients and organic matter. Alternatively, the low P concentrations in the Elwha sediments may be due to low P concentrations in incoming material. There are no major polluters in the ONP, leading to low inputs of nutrients into the Elwha River (Munn et al. 1999). My study found low C and N concentrations in the sediments, indicating that the organic matter and thus the organic P is probably low for this system.

The Elwha sediment types differ from each other. The delta sediments, which are fine sand, have lower concentrations of each of the three P fractions than the lake sediments, which are mostly silt (Tables 2 and 3). This supports Hypothesis 1, which states fine sediments have higher concentrations of P versus the coarse sediments. Size classes smaller than coarse silt fractions have the highest affinity for P (Huijun et al. 2010). The higher Fe~P in the lake sediments is consistent with their higher amorphous Fe (Table 3). The higher organic P in the lake sediments is consistent with the higher concentration of C (Table 4).

The implications of this are very important for the Elwha ecosystem response to dam removal. The smaller particles are lighter and more likely to be resuspended after the dams are removed, compared to the larger particles. The smaller particles will be swept out of the reservoir, potentially depositing them on the flood plain, or into the Strait of Juan de Fuca. This implies that the particles with the most P are most likely to leave the system. The larger, heavier particles are more likely to be left in the reservoir or on the flood plain. For plant and algal growth, the large particles will provide even less biologically available P than the smaller, more mobile particles, thereby limiting biological activity. By limiting excess algal

growth there may be few water quality problems, but poor sediment nutrient quality will prevent growth of plants for bank stabilization.

5.2 Isotherm Study

The isotherm study shows the quantity of P immobilized upon addition of P. The reason for the P removal could be the sediments' andic properties. The andic properties of some soils allow for the adsorption of P onto Fe and Al oxides in large quantities (Buol et al. 2003, p. 80, p. 236). This is unrelated to Ca~P or microbial uptake. The lake sediments were found to have lower water concentrations of P compared to the delta sediments after the two-week incubation. However, both sediments removed 99.99% of added P from solution. The lake sediments maintained around 10 µg P/L, while the delta sediments maintained around 50 µg P/L in solution. These values are similar to the values found by Munn et al. (1999) of 10-20 µg P/L. The similar concentrations of P between my study and the Munn et al. (1999) study could suggest that the adsorption of P by the sediments could be regulating the concentration of P in the water column. Baldwin (1996a) had initial isotherm P concentrations of 100, 1000, or 10000 µg P/L and found equilibrium concentrations of P to be between 0 and 10000 µg P/L. There were 11 sites studied with varying degrees of sediment exposure to air, but all were within the same reservoir, Chaffey Reservoir, Australia. The different equilibrium values of P were due to the different sediment sites and their corresponding exposure histories. The sediments with the most exposure to air were the sediments with the most P found in solution at equilibrium. In my study, only small amounts of P were left in solution at the end of the two weeks, but the higher concentration in solution for the delta sediments could be due to previous drying conditions.

5.3 Incubation Study

The concentration of SRP at any point in time is the result of many release and immobilization processes (Fig. 2). The incubation study determined the net result of these processes under different salt concentrations, atmosphere types, sediment types and time. The response of SRP was often the consequence of interaction among these factors (Fig. 5).

5.3.1 Atmosphere Types

Different atmospheres were used in the headspace of the incubation tubes to affect the redox potential of the sediments. The redox potential has a potentially huge effect (see Section 2.4.2) on the release/immobilization of P, with lower redox potential causing Fe dissolution and P release from Fe~P and higher redox potential causing Fe precipitation and P immobilization. However, the incubation study found that the atmosphere type (air or N atmosphere) did not have an effect on P release (Fig. 4). These findings are contrary to Hypothesis 2, which stated exposure of sediments to oxic conditions would decrease P release into water.

The simplest explanation for lack of response is that the administration of the atmosphere treatments was not enough to cause differences in redox potential between the two atmospheres. The incubation lasted two weeks, and the sediments were analyzed at the beginning and the end of the incubation. If the sediments had a very negative (low) redox potential, two weeks might not be enough time to alter the prevailing redox potential. A similar study (Gunnars and Blomqvist 1997) incubated their sediments for a mere eight days and found released P, Fe and Mn under anoxic conditions and substantially less released P and no Fe or Mn under oxic conditions. The anoxic and oxic conditions in the Gunnars and Blomqvist were simulated in a similar way compared to my study. Nitrogen and air were

bubbled constantly through the Gunnars and Blomqvist samples, instead of being exposed to once a day in my study. The Elwha sediments may not have had enough time or exposure to air/N to change the redox potential. Gächter and Wehrli (1998) suggest that focusing on dissolved oxygen concentrations as the only controlling mechanism for P release is wrong and that there are several other variables that may be of critical importance.

The oxygen or N atmospheres did not alter amorphous Fe control of P. Perhaps the concentration of amorphous Fe was so high that the N atmosphere only reduced a fixed concentration of Fe(III) to Fe(II). Or, there is plenty of amorphous Fe to dissolve without releasing much P because there is little Fe~P.

Golterman (1998) suggests that with higher concentrations of Ca in solution, higher amounts of P will bind to Ca, whatever the atmosphere type may be. Ca~P is pH dependent; lower pH levels will dissolve the Ca~P complex, and lower pH levels will be present under high levels of photosynthesis and low redox potential (Golterman 2001). The redox potential will lower the pH through the anaerobic decomposition of organic matter producing CO_2; which then turns into carbonic acid (Golterman 2004, p. 42). If the sediments are heavily influenced by Ca instead of Fe and the N atmosphere or low redox potential did not lower the pH, then it can be assumed that atmosphere may not have a large effect on P release. This is realistic given that there was very little organic matter to decompose anaerobically and thus limited source of carbonic acid to change the pH.

5.3.2 Salt Concentrations and Time

Salt concentrations of the water column are important to consider if the sediments are transported to the Strait of Juan de Fuca from the reservoirs. The smaller sized, lake bottom particles will travel further than the larger, heavier, delta particles. Ligand exchange between

dissolved anions and Fe~P might play an important role in P release upon sediments entering the Strait. My study indicates that saltwater did not increase P release. This is contrary to Hypothesis 3, which states exposure of sediments to saltwater increases P release into water. Jordan et al. (2008) state that the main factor controlling P release in marine waters is the presence of sulfides that reduce and break up Fe~P. Given that my study likely did not have concentrations of sulfides sufficient to reduce the Fe~P complexes, little P was released under saltwater conditions. Jordan et al. (2008) found an increase in OP and SRP with increased salinity. An increase in OP would occur under conditions where SRP is taken up by biota and incorporated into cellular processes. In my study, if P was released under marine conditions, it could have been taken up by the biota living in the sediment samples, preventing the actual amount of P release to be determined. The Ca~P in my sediments are probably influenced by the changes in pH. Unfortunately, the pH of the saltwater and freshwater was not measured, but future studies could provide information on SRP release from Ca~P between the two water types.

5.3.3 Sediment Type and Time

The lake and delta sediments differ in their concentrations of P fractions, amorphous Fe, C, N, and particle size. They also differ in the temporal response of P release in freshwater. Phosphorus release increased in delta sediments over time, but remained constant in lake sediments (Fig. 5). The lake sediments must have reached equilibrium quickly compared to the delta sediments. The delta sediments released more P over time, indicating that the sediments were in the process of coming to equilibrium with the water column by releasing P.

The saltwater sediments are also coming to equilibrium, but the equilibrium has changed with the introduction of salts. In saltwater, P release from both sediments increased over time because the bound P is coming into equilibrium with the water column, releasing more over time.

5.3.4 Integration of Processes

The complex behavior of P released in the incubation suggests that multiple processes are involved in controlling P dynamics. The following is a plausible explanation of the factors influencing P release as displayed in Fig. 8. The P released in sediment–saltwater suspensions at 4 hours is the result of displacing and diluting the initial porewater. Porewater concentrations were 32 µg P/L for delta sediments and 16 µg P/L for lake sediments. These were calculated as P released (µg P/kg dry sediment) x (kg dry sediment/L porewater), where the latter term is from moisture content analyses. The higher porewater concentration of the delta sediments is consistent with its higher isotherm equilibrium SRP concentration at around 20 µg P/L compared with lake sediments at around 10 µg P/L (Fig. 6). I expect the porewater to have been in equilibrium with the sediments, because of the 6-month storage of the moist sediments prior to the incubation. The similarity of estimated porewater SRP concentrations and isotherm equilibrium SRP concentrations provides support that the P released in saltwater suspensions was from porewater displacement and dilution.

The P released in freshwater at 4 hours may be the result of lysis of microbial cells via osmotic pressure upon contact with pure water, thereby releasing SRP, a process that did not occur in the saltwater. Compared with lake sediments, the lower organic P of the delta sediments (Table 3) likely indicates less initial microbial P and, consequently, less P released

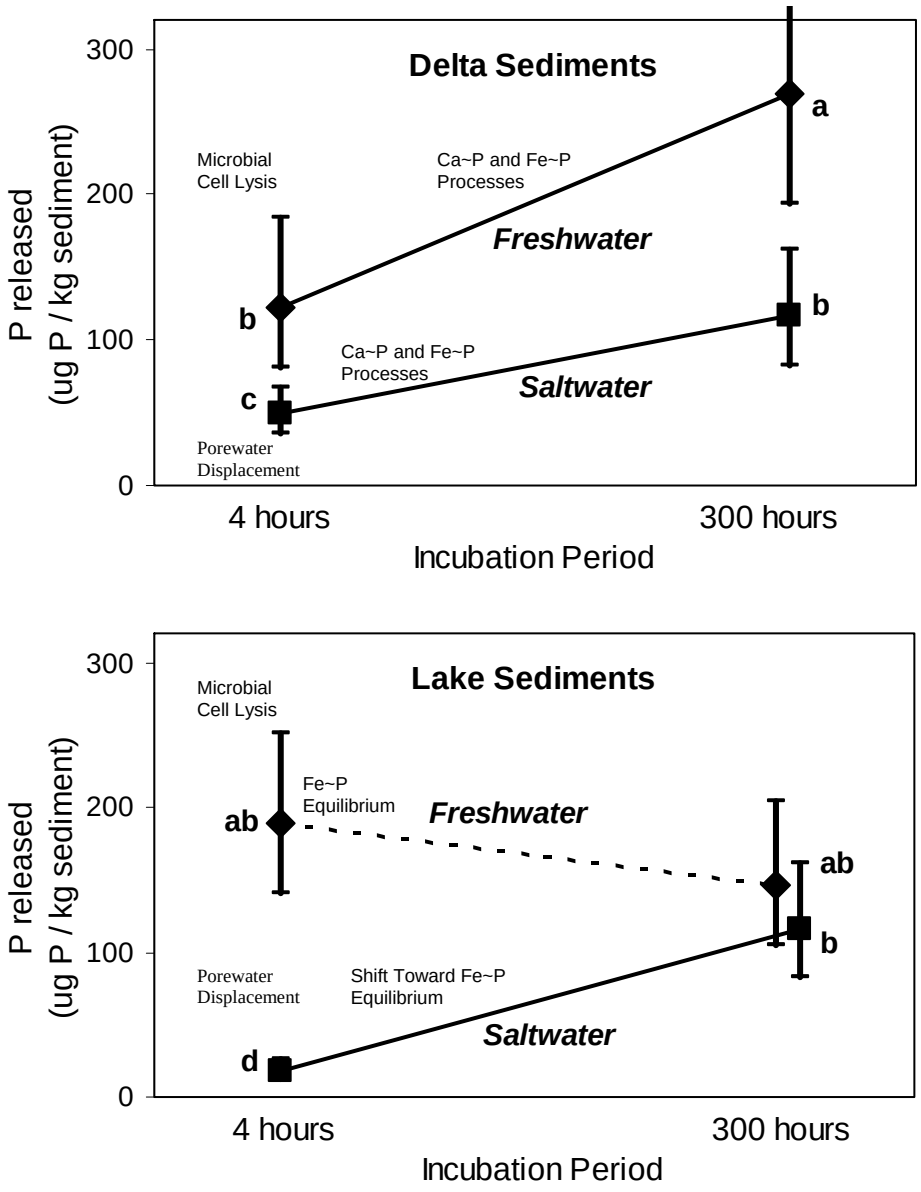

Figure 8. Plausible explanations for P release patterns from incubation study. The main processes are porewater displacement, microbial cell lysis, maintenance of Fe~P equilibrium, shift toward Fe~P equilibrium, Ca~P and Fe~P processes.

from it. If the delta sediments did have a microbial population, then due to the changing delta conditions of flooding and exposure to air, the microbe population could be resistant to changes and less likely to lysis (Surridge et al. 2007). This would explain the lower initial concentrations of P in the delta, freshwater sediments.

At 4 hours, the high P released of lake–freshwater suspension resulted in an SRP concentration that was in equilibrium with respect to Fe~P reactions, and there was no change in P released over the next 296 hours. At 4 hours the other suspensions were out-of-equilibrium with respect to Fe~P reactions. Between 4 and 300 hours, the lake-saltwater suspension increased the P released as the suspension approached the same equilibrium as the lake-freshwater suspension. Ligand exchange may have occurred, with SO_4^{2-} or Cl^- replacing orthophosphate and increasing P released with time. Spiteri et al. (2008) reports that the release of P from saltwater immersed sediments needs to overcome the adsorption of P onto Mg^{2+} ions to form Mg-phosphate surface complexes. The lower rates of P release in salt water on the Elwha sediments could be result of Mg binding.

In delta sediments, P release increased in both saltwater and freshwater between 4 and 300 hours, but the two water types did not converge on a common equilibrium point like the lake sediments did. Perhaps reactions with Ca~P, as well as Fe~P, are instrumental in their different behaviors. Surridge et al. (2007) reported a higher concentration of P in an incubation of deionized water compared to reconstituted river water in peat. They suggest that this P release is due to the reduction of Fe~P and thus the release of P without the sulfate reduction of Fe~P. The release of P from the Elwha sediments in the nanopure water could be a result of the reduction of Fe~P and not the reduction of S and Fe~P.

6.0 Conclusion

6.1 Application of Elwha River Sediment Analysis Studies

This study provides information to managers of the Olympic National Park about sediment characteristics and the potential for sediments to supply P for algal growth in water and vascular plant growth on exposed sediments. It allows forecasting about the response of P to dam removal.

Dissolved P concentrations are unlikely to increase sufficiently to cause water quality problems. For example, in the 1994 Lake Mills drawdown experiment, the highest concentration of suspended sediments was 6000 mg P/L (Childers et al. 2000). If the maximum P release occurred from these suspended sediments (300 µg P/kg, Fig. 5) it would equate to an increase in dissolved P of ~ 2 µg P/L. The increase in P concentrations is unlikely to influence P concentrations in the river water because the river water is flowing and unlikely to be in equilibrium with the sediments. Increased mixing after dam removal will likely cause dilution of P concentrations in porewater that has come into equilibrium with the sediments.

The smaller particles of sediment could be transported to the nearshore environment. The marine environment is not necessarily P limited, but the incoming sediments might change the degree of availability. If large quantities of the sediments make it to the marine environment where the sediments could immobilize P this could potentially affect productivity.

The nutrient quality of the Elwha sediments is fairly poor. The concentrations of C, N, and P are low. The P present is not likely to be readily released given the sediments' capacity

to adsorb P, as indicated in the isotherm study. The incubation study indicates that P is present, but in small quantities and could hinder plant growth.

Some larger sediments will be eroded, transported and deposited in the river channel or on floodplains, but the majority is predicted to remain in the reservoirs (Mussman et al. 2008). The sediments remaining in the reservoirs will have limited P availability, decreasing the likelihood of bank stabilization through plant growth. Floodplain plant growth will also be limited on deposited sediments due to low concentrations and availability of P. After the dams are removed fertilization of exposed or transported-and-deposited sediments may be necessary to establish vegetation for sediment stabilization. Fertilization may provide a source of N and K, but P may still be limited because of the high P immobilization capacity of the sediments, unless plant or microbial released P is substantial. Plants have the ability to extract some P through the root-mediated decrease in pH. The production of H^+ can release P from Ca~P, and H^+ production has been shown to happen in P-limited circumstances (Hinsinger et al. 2002). Phosphorus can also be extracted through the release of carbonic acid by both plants and soil microorganisms creating a low pH environment (Sylvia et al. 2005 p. 471). Plants could access P through the acidification of the rhizosphere in Elwha sediments as long as the mechanism for acidification is present.

6.2 Future Studies

The sediments should be further tested for pH, Eh, Ca, Fe, S, and Mn. The pH and Eh of the sediments will increase understanding about the Elwha sediments and the potential for nutrients to be bioavailable. The analysis of the Elwha sediments for Ca, S and Mn will give a better understanding of how the sediment concentrations relate to the forms of P and the release of P. The sediments need to be analyzed for Ca in order to determine why my study

found such large concentrations of Ca~P. Analyzing the sediments for different forms of Ca would be useful to determine under what conditions P will be released or immobilized. Analyzing for S would be useful in determining Fe, S and P interactions, as suggested by Gunnars and Blomqvist (1997).

A longer incubation could lead to a clearer understanding of the influence of oxygen exposure on P dynamics and how the response varies with sediment type. While no response to oxygen was observed in 300 hours, longer exposure to oxygen may influence Fe solubility and adsorption of P. Longer incubations might also better differentiate the responses of the coarse versus fine sediments

6.3 Concluding Remarks

The Elwha River sediments from Lake Mills have limited P available for algal and plant growth. The water quality after the dams are removed is unlikely to be harmed by the release of excess P. Plant growth on Lake Mills sediments may be constrained by the low concentrations and limited availability of P. Although fine lake bottom sediments had higher concentrations of P fractions than coarse delta sediments, there were only minor differences in P release during incubation. In contrast, the lake sediments immobilized more added P and maintained dissolved P at lower concentrations. Contrary to expectations, short-term exposure of sediments to oxygen did not influence P release, and exposure to saltwater did not increase P release.

These findings are important and unique to the Elwha River. They uncover the different fractions of P in the sediments and reveal the potential response of sediment-bound P to different environmental conditions. The incubation is a novel method for examining the potential responses of sediment-bound P and could provide a model for other researchers

when studying sediment bound P. The characterization study complements the incubation study and gives insight as to the reasons for different ways of releasing and immobilizing P in the Elwha River. Managers of the Elwha River and the Olympic National Park could use the information found in this study to better understand the ecosystem response to the removal of the Elwha River Dams.

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Appendix

Inorganic Phosphorus Analysis of Elwha River Sediments from the Lake Bottom and Delta

Table 6. Inorganic P fraction [mean (95% CI)] of delta and lake sediments from Lake. n = 4 locations per sediment type.

Sediment	Inorganic P‡
	— mg / kg oven dried sediment —
Delta	780 (653–908)
Lake	905 (617-1192)
P†	0.255

† P value from 2-sample test

‡ Geometric mean and 95% CI back-transformed from log-transformation.